Transport Properties and Kinetic Theory

A relevant note about Egypt Air

Transport Properties

Motions inherent in materials at a molecular level even at equilibrium

Kinetic and Molecular Theory of Gases

Molecular Collisions

Classical Thermodynamics and Molecules

Up until this point we have largely been discussing early 19th Century Science

Materials had bulk properties.

They were essentially considered as continuum materials.

And with the exception of a brief discussion of Entropy, the particulate nature of matter was not fundamental to the theories and derivations (amounts were though).

We will now transit rapidly through the last half of the 19th Century and into the twentieth.

Development of the Atomic Theory

5th Century B.C.E.-	Leucippus of Miletus	
430 B.C.E.	Democritus of Abdera	*atomos*
	atoms were uniform, solid, hard, incompressible moving in infinite numbers through space until stopped Different sizes and shapes led to different matter	
~300 B.C.E.	Epicurus of Samos	gods subject to natural law

Aristotle destroyed these theories on “Philosophical” grounds.

And then…..centuries.

1649	Galileo Galilei	vacuums
1658	Robert Boyle	Boyle’s Law
~1700	Isaac Newton	Classical Atomic Theory

Development of the Atomic Theory

1738	Bernoulli	The Kinetic Theory
1794	Joseph-Louis Proust	Law of Definite Proportions
1800-1803	John Dalton Why don’t heavier gases sink to the bottom, and lighter gases to the top?	REAL Atomic theory.
1810-12	Dalton and Avogadro	Molecular Theory
1827	Robert Brown	Pollen Experiments
1851-1857	Joule and Clausius James Clerke Maxwell Ludwig Boltzmann	Further Kinetic Theory Velocity Distribution of Gases Entropy and the Kinetic Theory

Boyle (1662): Static vs. Kinetic

Boyle argued that the properties of gases were due to stationary, compressible particles.

- static contiguous particles at rest
- must be compressible, like pieces of wool
- if not touching then must be variable in size or in motion
- static explanation does not account for ability to expand to fill any container
- must then postulate that particles are self repulsive, which is consistent with caloric theory

8.2. Daniel Bernoulli (1738)

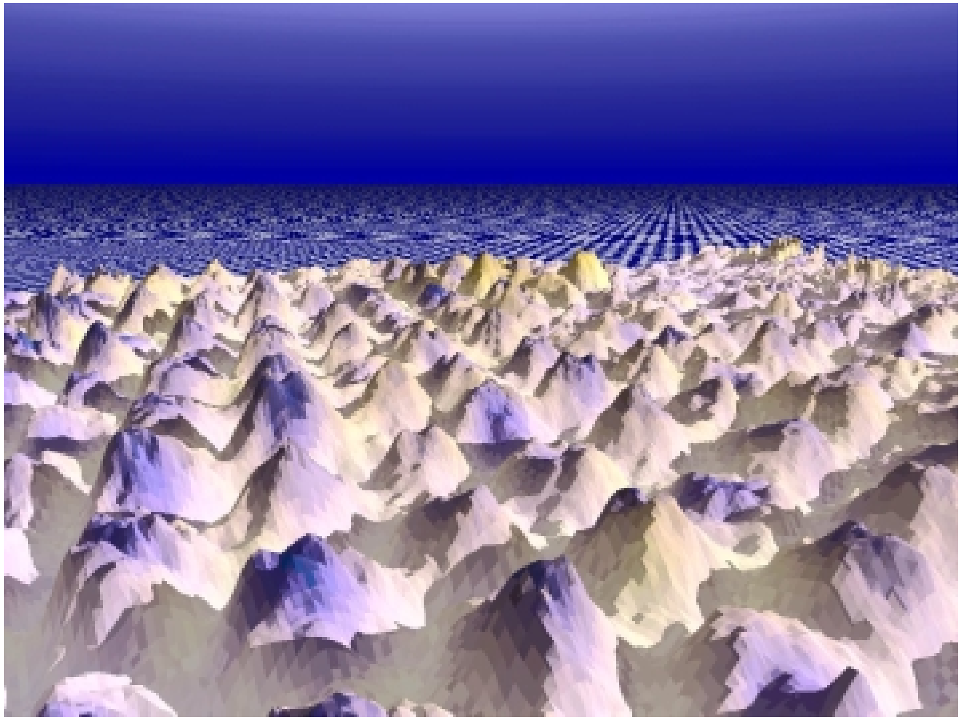
deduced Boyle's Law using Newtonian mechanics

- anticipated kinetic theory of gases
- views were too advanced for his time
- about three generations too soon
- idea died for lack of attention
- two important contributions to scientific thought
- recognized the equivalence of heat and mechanical energy through particle motion
- conceived the possibility that a quantitative relationship (Boyle's law) could be induced from the chaotic picture of randomly moving particles

Evidence for the Atomic Theory

Modern evidence includes:

Molecular beam work
AFM
Single Molecular Microscopy
Laser Tweezer Studies



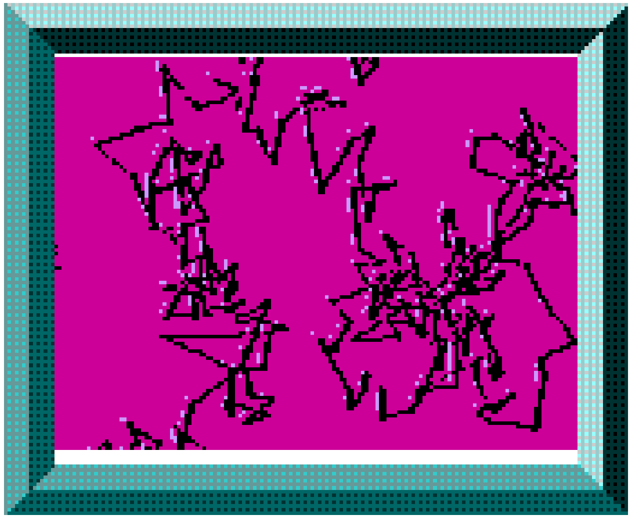
Brownian Motion

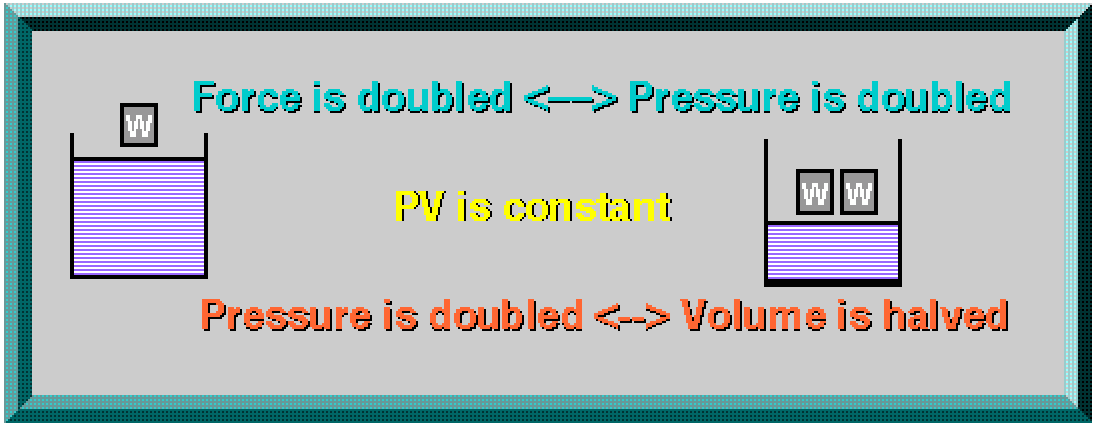
One of the most compelling examples for the atomic and kinetic theories of matter was the observation of Brownian Motion.

A small pollen particle seems to bounce around at random in fluid solution.

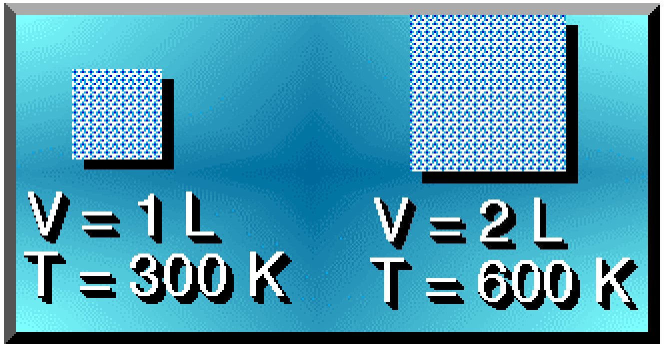
How could this work?

Einstein worked in out in 1905.





Boyle's Law
PV= const.

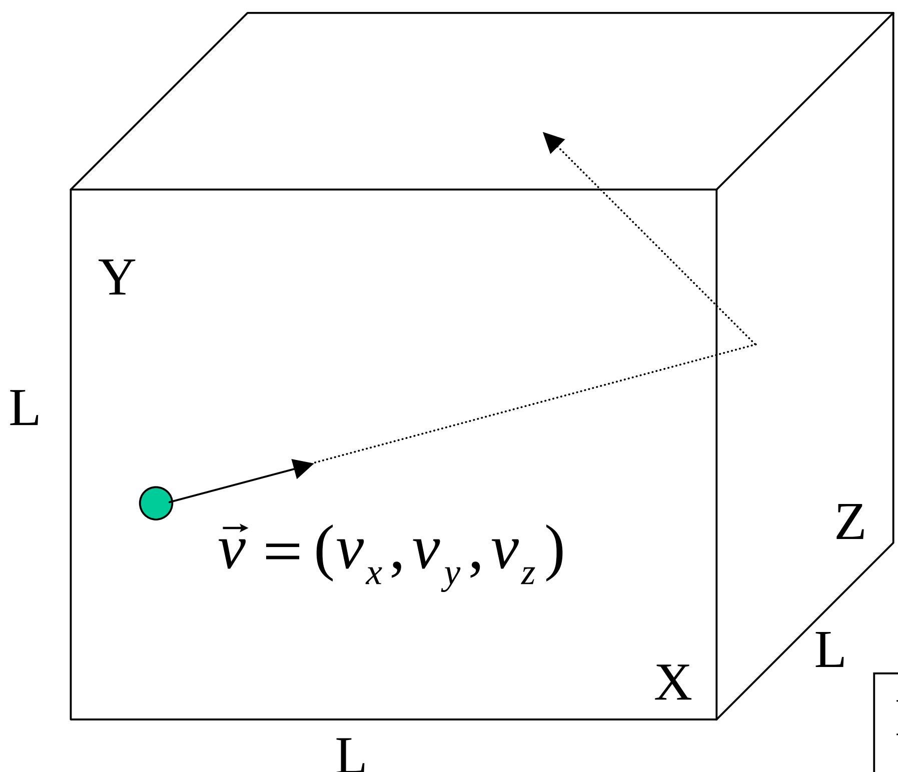


Charle's Law
V/T = const.

From observations like Brown's, and relationships like these the atomic and kinetic theories were deduced and validated!

We want to be able to relate the macroscopic variables of Pressure and Temperature to the molecular nature of matter. From here we can get to thermodynamics.

So we start with the following thought problem:

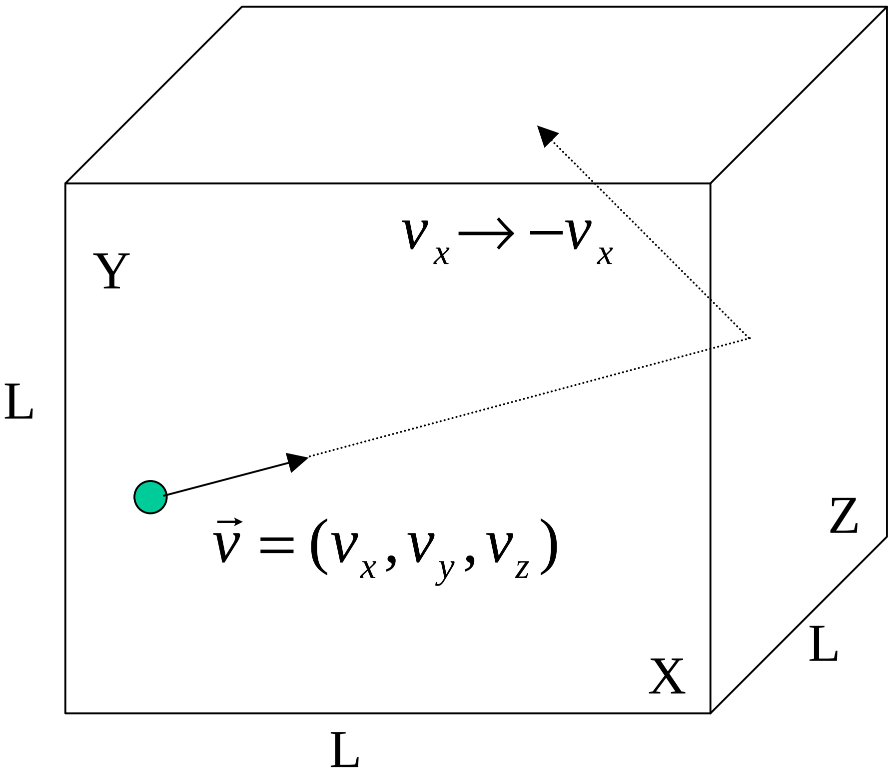


We assume:

1) Gases are composed of particles
2) Particles are in constant motion
3) Collision w/ walls --> Pressure
4) Collisions w/ walls are elastic
5) Large distances btw particles

6) Particles are point mass
7) No strong forces btw particles
(Elastic collisions)

In a gas: the distance between particles is about 10 times the molecular diameter



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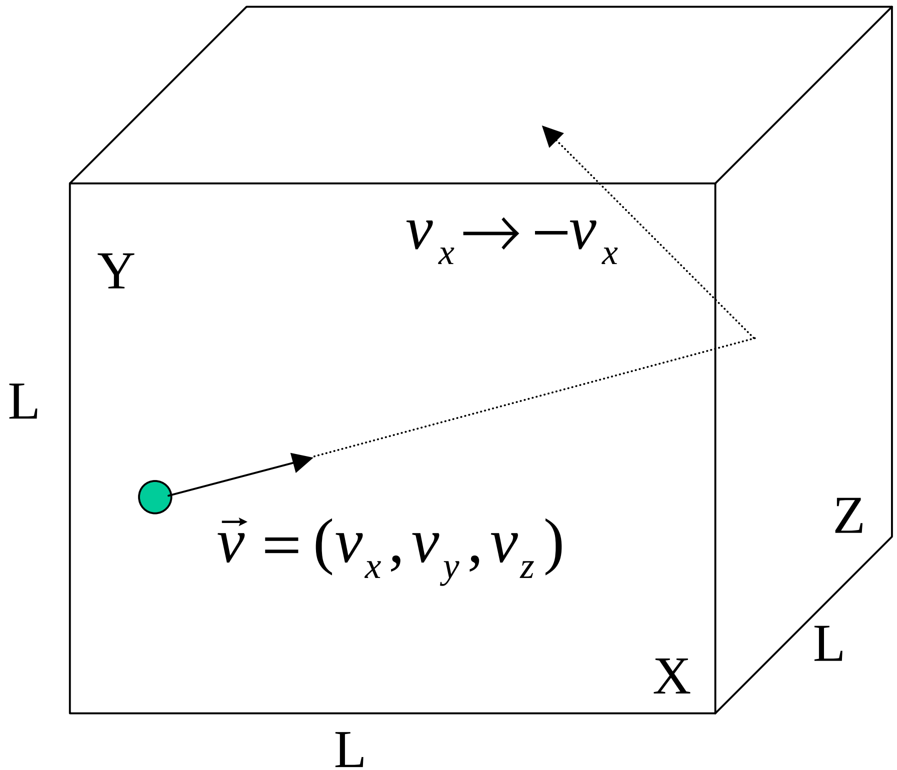
Elastic collisions means that the direction of a particular component of velocity changes sign but not magnitude.

$$\|\vec{v}\| = v_x^2 + v_y^2 + v_z^2$$



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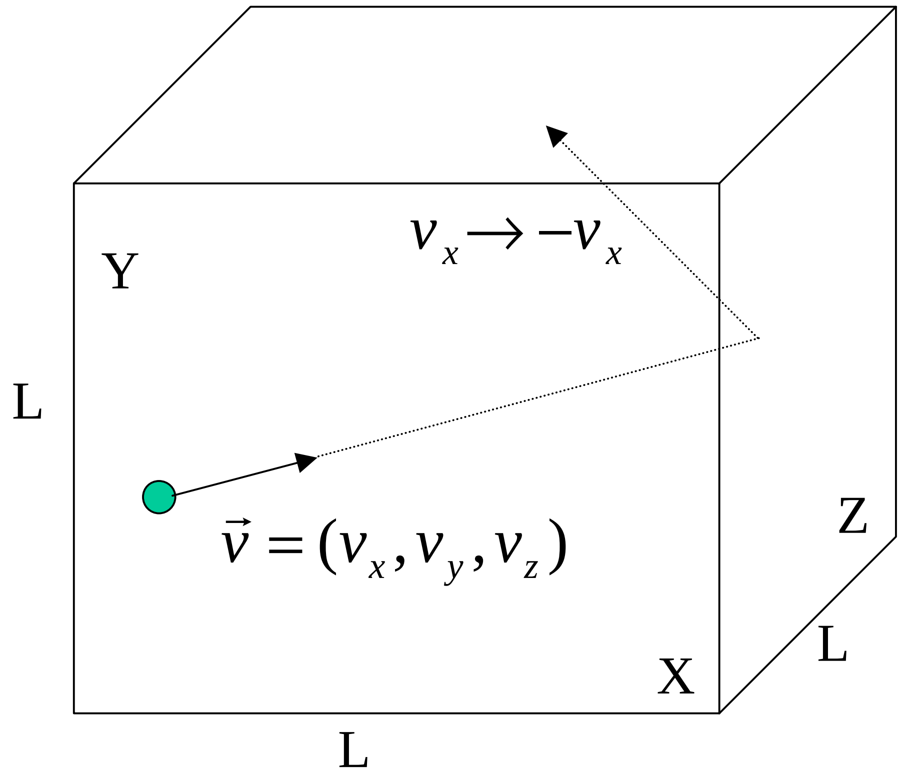
Since every reaction has an equal an opposite reaction the momentum transferred to the wall is:

$$\Delta p = m * \Delta v_x = 2 * m * v_x$$



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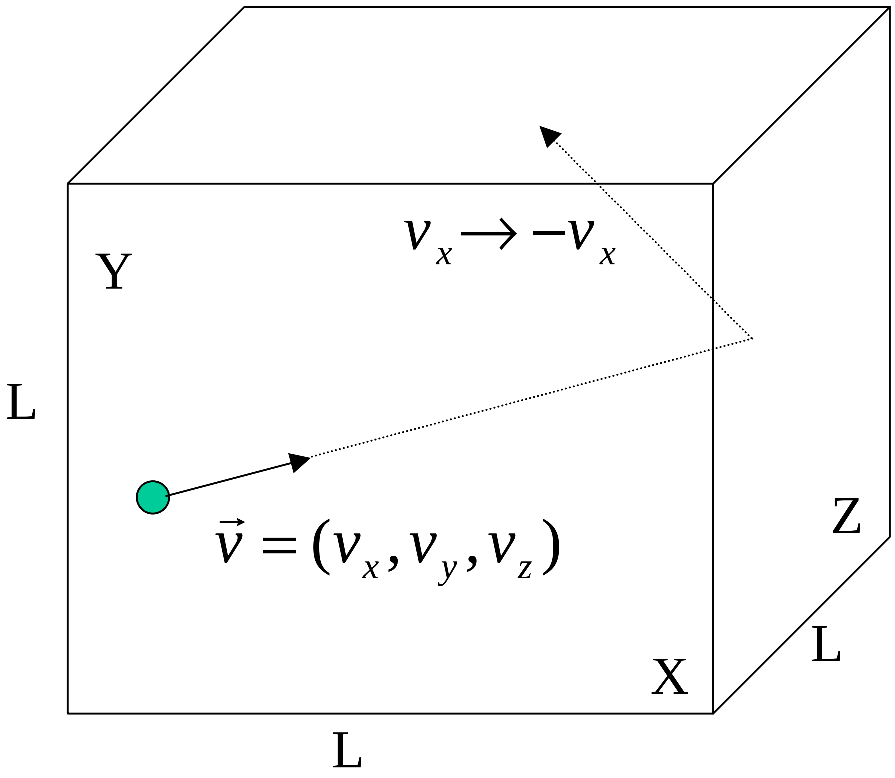
Now the number of collisions per unit time may also be calculated:

$$N_{collisions} / time = v_x / L$$

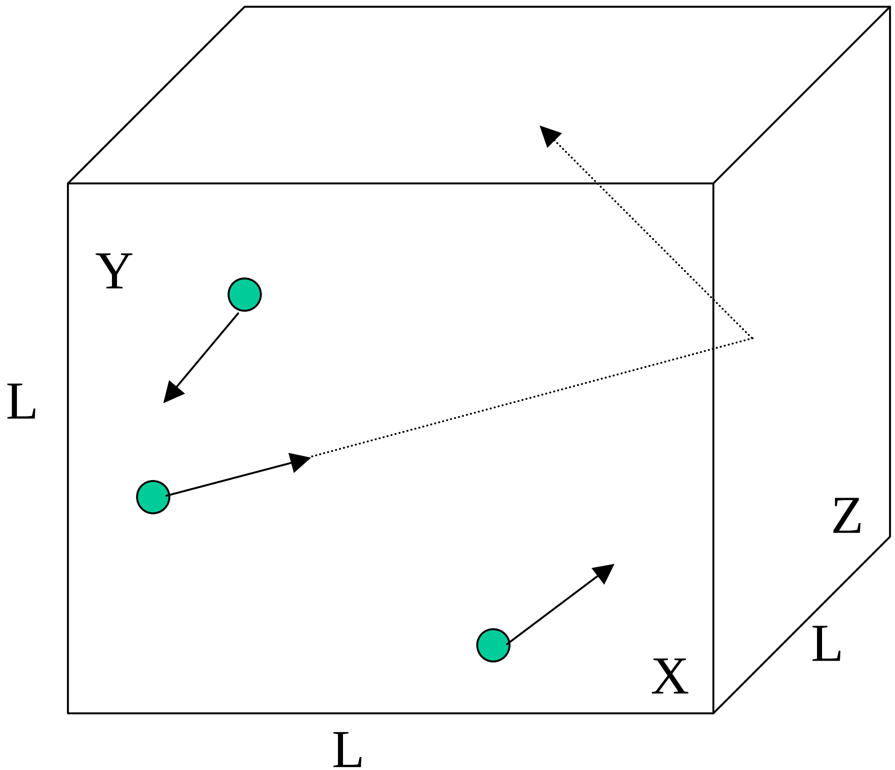


Therefore the total change in momentum per unit time can be given as:

$$\Delta p = m * \Delta v_x = 2 * m * v_x$$

$$N_{collisions} / time = v_x / L$$

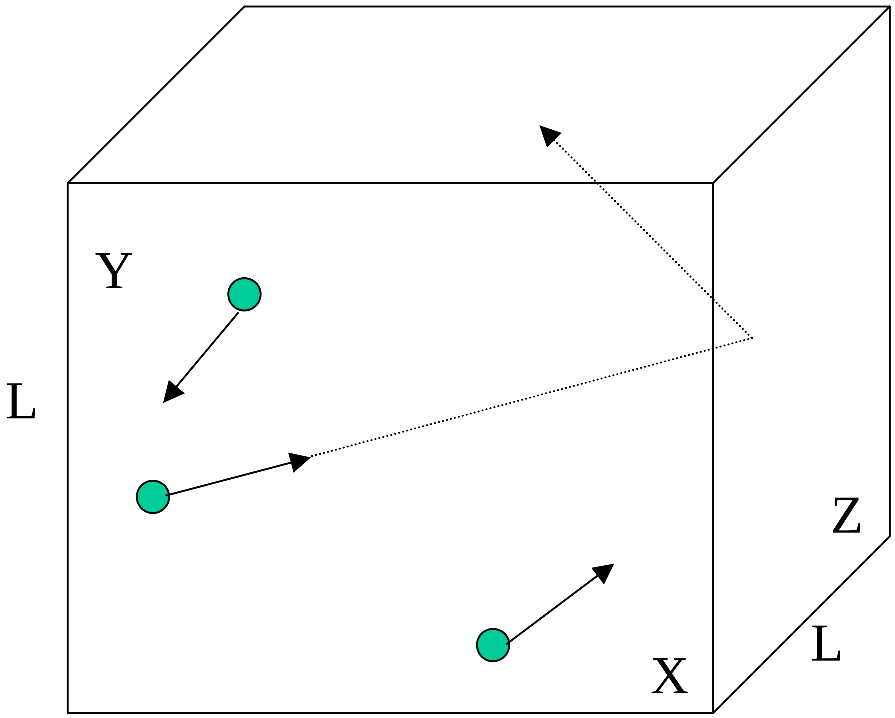
$$\boxed{\frac{dp}{dt} = 2 * m * v_x * v_x / L = 2mv_x^2 / L}$$



$$\boxed{\frac{dp}{dt} = 2mv_x^2 / L}$$

If the box contains N molecules we can average over the velocites and try and get the average change in momentum:

$$\langle v_x \rangle = \frac{\sum_{i=1}^{N} v_{x,i}}{N} \qquad \langle v_x^2 \rangle = \frac{\sum_{i=1}^{N} v_{x,i}^2}{N} \qquad \langle v_x \rangle^2 = \left(\frac{\sum_{i=1}^{N} v_{x,i}}{N} \right)^2$$

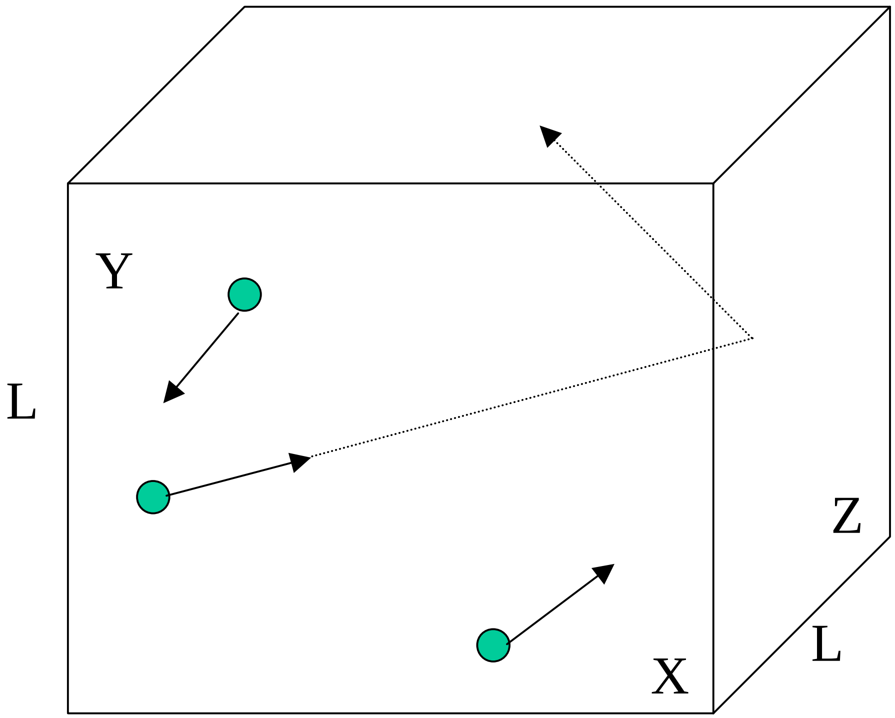


$$\frac{dp}{dt} = 2mv_x^2 / L$$

$$\left\langle v_x^2 \right\rangle = \frac{\sum_{i=1}^{N} v_{x,i}^2}{N}$$

$$\left\langle \frac{dp}{dt} \right\rangle = 2m\left\langle v_x^2 \right\rangle / L = Force$$

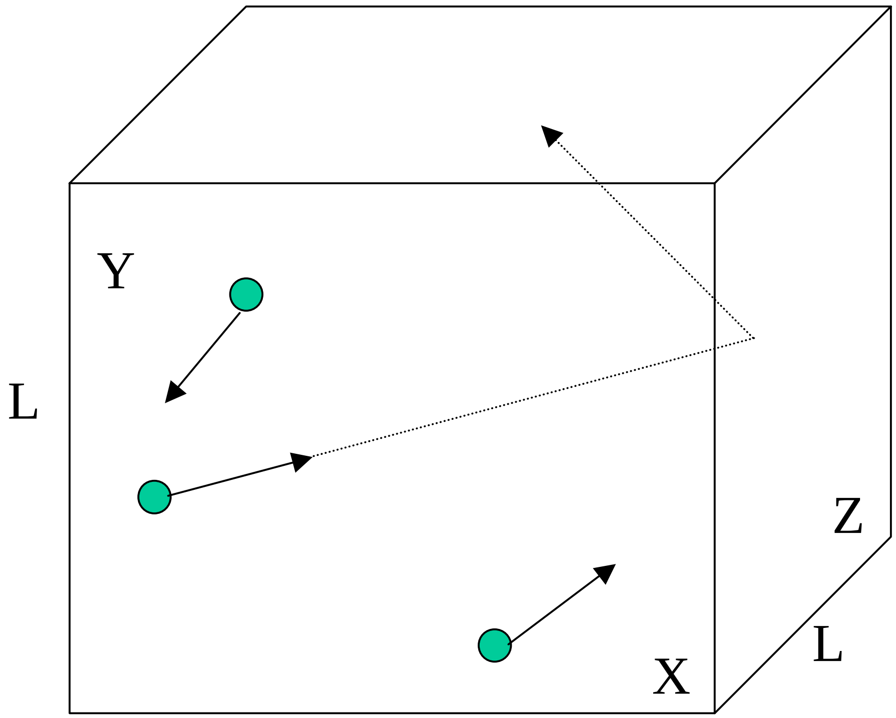
And Pressures is force/Area



$$\boxed{\left\langle \frac{dp}{dt} \right\rangle = 2m\left\langle v_x^2 \right\rangle / L = Force}$$

So pressure must be:

$$P = \frac{\left\langle \frac{dp}{dt} \right\rangle}{A} = \frac{2m\left\langle v_x^2 \right\rangle}{L * A} = \frac{2m\left\langle v_x^2 \right\rangle}{L * (2L^2)} = \frac{m\left\langle v_x^2 \right\rangle}{V}$$



$$P = \frac{m\left\langle v_x^2 \right\rangle}{V}$$

Since there is no directional bias here

$$\boxed{\left\langle v_x^2 \right\rangle = \left\langle v_y^2 \right\rangle = \left\langle v_z^2 \right\rangle = \frac{1}{3}\left\langle v^2 \right\rangle}$$

$$\boxed{P_{tot} = \frac{Nm\left\langle v_x^2 \right\rangle}{V} = \frac{Nm\left\langle v^2 \right\rangle}{3V} = \frac{nM\left\langle v^2 \right\rangle}{3V}}$$

Now we have to relate this to temperature. We can do so through kinetic energy.

$$\boxed{P_{tot} = \frac{Nm\left\langle v^2 \right\rangle}{3V}}$$

We know from basic physics that:

$$\left\langle U_{translation} \right\rangle = \frac{1}{2} m \left\langle v^2 \right\rangle = \frac{3}{2} kT$$

Which allows us to prove Boyle's Law!

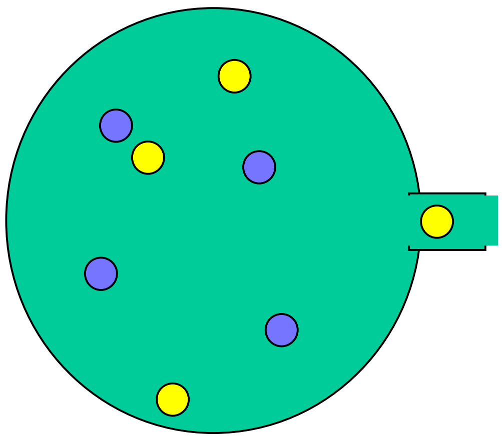
$$\left\langle U_{translation} \right\rangle = \frac{1}{2} m \left\langle v^2 \right\rangle = \frac{3}{2} kT$$

$$\boxed{P_{tot} V = \frac{Nm\left\langle v^2 \right\rangle}{3} = \frac{2}{3} N \left\langle U_{translation} \right\rangle}$$

For an ideal gas then we can immediate find a relation between the translational kinetic energy and the temperature.

This also leads us to Graham's law of Effusion:

The rate of diffusion of a gas is inversely proportional to the square-root of its mass.



In a mixture of two gases…the temperature of the two gases must be the same!

$$\left\langle U^{blue}_{translation} \right\rangle = \left\langle U^{yellow}_{translation} \right\rangle$$

$$\frac{1}{2} m_{blue} \left\langle v^2_{blue} \right\rangle = \frac{1}{2} m_{yellow} \left\langle v^2_{yellow} \right\rangle$$

$$\frac{\left\langle v^2_{blue} \right\rangle}{\left\langle v^2_{yellow} \right\rangle} = \frac{m_{yellow}}{m_{blue}}$$

Can be used to separate isotopes!

Homework:

Reading Chapter 6: 255-268
TSW 5.16,5.17,5.24,6.1,6.2